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(54) Isooctene production

(57) Foaming in the stripping tower during removal of unreacted butenes from isobutene dimer formed by the sulphuric acid dimerisation of C₄ is reduced by reducing the butadiene content of the initial C₄ stream to below 0.3 wt% by selective hydrogenation.

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SPECIFICATION

Improvements in or relating to isooctene production

- 5 The present invention relates to improvements in or relating to the extraction and dimerisation of isobutene by sulfuric acid. 5
- Isobutene in C4-streams from refineries and steam-crackers can be dimerised in the presence of sulfuric acid to produce mainly isooctenes which may then be used as gasoline components or chemical intermediates. After extraction of isobutene by sulfuric acid, the adduct is heated to
- 10 form the dimer, the sulfuric acid being recycled after separation. Caustic is then added to the raw dimer to neutralise traces of acid and saponify the byproduct esters of sulfuric acids. At the same time unreacted butenes are steam stripped. After separation of the dilute caustic the isooctenes are distilled to remove polymerised compounds. 10
- This process has two major problems, firstly certain compounds such as organic sulfones, sulfones, sulfates and sulfonates are produced as byproducts of the sulfuric acid treatment of the C4-stream and these materials being surfactants tend to cause foaming in the stripping tower, at times rendering the tower inoperable. Costly antifoaming agents must be used to overcome this situation. 15
- Secondly the spent caustic must be disposed of. The presence of these surface active agents leads to the formation of emulsions which in turn leads to disposal difficult as settling of flocculants like ironhydroxide is inhibited. 20
- A typical C4 feed for the above reaction comprises:
- | | | | |
|-----|-----|-------------------------------|----|
| 0.1 | to | 5 wt% of isobutane | |
| 25 | 0.1 | to 10 wt% of n-butane | 25 |
| | 5 | to 50 wt% of isobutene | |
| | 10 | to 60 wt% of 1-butene | |
| | 5 | to 30 wt% of 2-butene (trans) | |
| | 1 | to 20 wt% of 2-butene (cis) | |
| 30 | and | | 30 |
| | 0.3 | to 2 wt% of 1,3-butadiene. | |
- We have found that the presence of the butadiene in this feed makes a significant contribution to the presence of the surfactants which are then responsible for the foaming in the stripping tower, the organic phase in the spent caustic and the inhibition of settling of flocculants. 35
- According to the present invention thereof, the C4 feed stream is subject to a mild hydrogenation to hydrogenate the butadiene mainly to butenes prior to the treatment with sulfuric acid. We have found that if the butadiene content of the stream is reduced to below 0.3 wt% preferably to below 0.1 wt% the problems of foaming and caustic disposal are substantially eliminated. 40
- The selective hydrogenation of butadiene in butene streams is a known technique for example as is described in 'Hydrocarbon Processing, Sept. 1978, p. 134'. We have found such a process using a supported palladium catalyst to be particularly useful in our invention. Our preferred conditions being hydrogenation in the gas phase using a hydrogen/butadiene molar ratio of 1-5, a pressure of 5-15 bar and a temperature of 70-100°C. 45
- We have found that this hydrogenated C4 stream may now be subjected to the standard sulfuric acid treatment to dimerise isobutene and that providing the butadiene content of the stream is reduced to below 0.3 wt% preferably below 0.1 wt% it may be subjected to the normal stripping and settling techniques to separate the disobutene dimer without problems of foaming during stripping or inhibition of flocculation during caustic disposal. 50
- The reason why the elimination of the butadiene gives the improvements is not fully understood but it is believed that the butadiene may copolymerise with other olefins in the presence of sulfuric acid to form oligomers which are then sulfonated by the sulfuric acid to yield detergent sulfonates. 55
- The formation of organic sulfates and sulfonates can also be explained via polysulfones or butadiene-sulfones as intermediate compounds. Several types of sulfones could be identified as well in the various isobutene dimer (isooctene) streams as in the spent caustic. The configuration of these sulfones is changed by heat treatment at about 150°C with or without caustic as it could be determined by infra-red and other suitable analytical methods. 60
- According to Houben-Weyl, Vol. IX (1955) 236/237 formation of polysulfones or cyclic butadiene sulfones is described by reaction of sulfur dioxide with butadiene. The so-formed sulfones are unstable and tend to react with other compounds. This explains the instability (gum forming tendency) of gasolines, containing unstabilized raw dimer.
- 65 Thus elimination of butadiene from isobutene streams by hydrogenation before dimerization 65

has the following advantages:

1. reduction of foaming in the tower where unreacted butenes are stripped with steam,
2. improvement of waste water quality.
3. improvement of thermal stability of the final isobutene dimer.

5 Whichever the correct mechanism(s) may be, we have found that the reduction of the butadiene content to a level of below 0.3 wt% preferably below 0.1 wt% reduces the quantity of anionic detergent in the spent caustic to about one seventh and, specifically the amount of sulfonates from 1400 mg/ltr to about 200 mg/ltr. 5

10 The present invention is illustrated by reference to the following EXAMPLE in which a C4-stream was fed to a sulfuric acid isobutene dimerisation unit over a period of several days and hydrogenation started during the middle of the period. 10

---The composition of the stream-before-and-after-hydrogenation was as follows:

15	Before hydrogenation	After hydrogenation	15
isobutane	0.4 wt%	0.4 wt%	
n-butane	2.3 wt%	2.9 wt%	
isobutene	33.9 wt%	33.7 wt%	
20 1-butene	42.2 wt%	41.9 wt%	20
2-butene (trans)	12.3 wt%	13.2 wt%	
2-butene (cis)	7.6 wt%	7.9 wt%	
1,3-butadiene	1.3 wt%	0.1 wt%	

25 Hydrogenation was achieved by passing a stream of a mixture of hydrogen and the C4-stream over a catalyst of palladium supported on alumina the mixture being such that 60 cubic metres of hydrogen and 8 liquid cubic metres of the C4-stream pass over the catalyst each hour. The system is held in the gas phase at 90°C under a pressure of 10.5 bar. 25

30 The sulfonates present in the spent caustic were isolated by preparative column chromatography, weighed and identified by determination of sulfur and their infrared spectrum, determined using a colorimetric test as described in 'Deutsche Einheitsverfahren zur Wasseruntersuchung, No. H 23'. According to this procedure, the anionics are reported as Tetrapropylenebenzenesulfonate (TBS). 30

35 The quantities as determined are shown in Table 1. 35

Table 1

40	Sulfonates mg/ltr	Anionics as TBS mg/ltr	40
Untreated feed	1366	2950	
Hydrogenated feed	222	378	

45 CLAIMS 45

1. A process for the production of iso-octene by the dimerisation of a C4 stream with sulphuric acid wherein the C4 stream is subjected to a mild hydrogenation to selectively hydrogenate butadiene present in the stream whereby the butadiene content of the stream is reduced to below 0.3 wt%.
- 50 2. A process according to claim 1 wherein the butadiene content of the stream is reduced to below 0.1 wt%. 50
3. A process according to claim 1 or claim 2 wherein the selective hydrogenation is effected in the gas phase over a supported palladium catalyst using a hydrogen/butadiene molar ratio of 1 to 5, a pressure of 5-15 bar at a temperature of 70 to 100°C.